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EFFECTS OF PLASMA AND OZONE TREATMENTS ON TENSILE AND WHITENESS PROPERTIES OF 100 % SILK

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Abstract: In this study raw and degummed silk fabrics are treated with low frequency oxygen plasma and ozone in order to investigate the effects on the physical properties of silk. Plasma and ozone treatments are performed individually and in combined order for 5, 10 and 15 min. The yellowness and whiteness values are determined after the plasma and ozone treatments. The tensile strengths of treated and untreated silk fabrics are measured. The SEM images of the surfaces of silk fabrics are investigated and the combined effect of ozone and plasma treatments are discussed after each test. Results indicate that there is more significant decrease in ozone treatment, considering decrease in whiteness indexes and increase in yellowness values of silk fabrics when compared to the plasma treatment. Generally, when the treatment time of plasma or ozone is increased, increase of yellowness and decrease of whiteness become clear.

Keywords: Low-frequency plasma, ozone, silk

%100 İpek Kumaşın Mukavemet ve Beyazlık Özellikleri Üzerine Plazma ve Ozon İşlemlerinin Etkileri

Özet: Bu çalışmada, plazma ve ozonun ipek kumaşın fiziksel özellikleri üzerindeki etkisini araştırmak amacıyla ham ve serisini giderilmiş ipek kumaşlar ozon ve düşük frekanslı oksijen plazma işlemlerine tabi tutulmuştur. Plazma ve ozon işlemleri birbirlerinden bağımsız olarak ve kombine olacak şekilde 5, 10 ve 15 dak. uygulanmıştır. Plazma ve ozon işlemlerinden sonra, sarılık ve beyazlık indeksleri belirlenmiş, kopma mukavemetleri ölçülmüştür. İpek kumaşların yüzeylerinin SEM görüntüleri incelenmiş ve her test ardından ozon ve plazmanın kombine efekti tartışılmıştır. Ozon ve plazma işlemleri karşılaştırıldığında, sonuçlar ipek kumaşların beyazlık indekslerinde azalışın, sarılık değerlerindeki artışın ozonlama işleminde daha belirgin olduğunu ortaya çıkarmıştır. Genel olarak, plazma veya ozonun işlem süreleri arttıkça sarılıktaki artış ve beyazlıktaki azalış daha net bir şekilde görülmektedir.

Anahtar kelimeler: Düşük frekanslı plazma, ozon, ipek

1. INTRODUCTION

Nowadays, apart from the basic requests of comfort and fashion, global trends in the textile industry demand functional textile products with high added value. Improving the properties of natural products has become increasingly important considering environmental impacts

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(Guohong et. al., 2011, Tieling et. al., 2012). Within this scope, silk, historically known as 'the queen of textiles'' is one of the most commonly used natural textiles because of its luxury and aesthetic appearance, soft handle, high wearing comfort, environmental and human friendliness, soft and smooth texture, excellent flexibility and mechanical strength (Guohong et. al., 2011,Tieling et. al., 2012, Chaiwong et. al., 2010,Guan et. al.,2009, Liu et. al., 2012). However, silk has inherent disadvantages such as problems in the dyeing process including weak color shade and high-loaded effluent, easy-wrinkling, deformation and even degradation caused by microorganisms, photo-induced aging and yellowing (Guohong et. al., 2011, Tieling et. al., 2012, Li et. al., 2012).

Silk is a kind of natural protein fiber consisting of 18 amino acids (R–CH [NH_2]–COOH) and it has various reactive functional groups including hydroxyl and amine groups (Tieling et. al., 2012). As seen in Fig. 1, it contains two structural fibroin filaments and these are coated with a family of glue-like sericin proteins, resulting in a single thread with a diameter of 10–25 μm (Li et. al., 2012, Sargunami and Salvakumar, 2006)

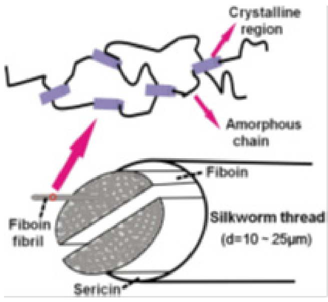


Figure 1:
The structure of silk (Li et. al., 2012)

Both fibroin and sericin, which account for about 75 and 25 wt.%, respectively, are proteins. Sericin includes a complex mixture of 5–6 polypeptides which widely differing in size, chemical composition, structure and properties, such as: solubility, hydrophility, and stickiness. The amino acid composition ranges from 16 to 38 mol% in the different sericins. The proteins form a sheath around the fibroin core during spinning of the silk filament. The physiological function of these proteins is to lower the shear stress and to absorb the water squeezed from the stretched fibroin mass during the process of fiber formation. Silk fibroin has an antiparallel, hydrogen bonded β-sheet and yields the X-ray diffracting structure called the "crystalline" component. Its chains are aligned along the fiber axis, held together by a close network of interchain hydrogen bonds. The adjacent -(ala–gly)n- sequences forming the well known-sheet crystals can be seen in Fig.2. The structure of fibroin is rich in glycine, alanine, and serine amino acids in the molar ratio 3:2:1, which form typical -(ala–gly)n- repeating motifs (McKee et. al., 2011, Freddi et. al., 2003).

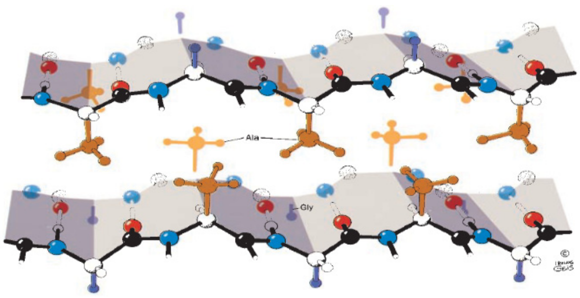


Figure 2:
Molecular model of silk fibroin (McKee et. al., 2011)

Sericin, a glue-like protein which contains glycine, serine, and aspartic acid, can be removed through a degumming process in order to allow the purification of the fibroin fibers (Li et. al., 2012, Sargunami and Selvakumar, 2006). Degumming is a process which silk fibers gain the typical shiny aspect, soft handle, and elegant drape highly requested by the consumers. While the fibroin is water-insoluble owing to its highly oriented and crystalline fibrous structure, sericin is readily solubilized by boiling aqueous solutions containing soap, alkali, synthetic detergents, or organic acids (Freddi et. al., 2003). In order to meet the corresponding demands of textile industry and to promote a wider utilization of silk fabrics, numerous attempts have been made in the surface modification and functionalization using a wide range of functional materials and technology during last decade (Li et. al., 2012). One of these processes among surface modification is the commonly used plasma treatment. Plasma includes a mixture of electrons, negatively and positively charged particles, neutral atoms, molecules and it's an electrically conducting and neutral medium, due to the equilibrium of the electrons and positively and negatively charged excited ions. The activated species, electrons and photons, are able to carry out physical and chemical reactions at the solid surface of textile materials via physical bombardment and plasma polymerization (Li et. al., 2012). Compared with conventional methods, plasma treatment has lots of advantages such as requiring lower chemical and energy consumption, no waste water, non-hazardous, dry, fast and environmentally friendly technique, non-utilization of solvents, no significant alterations in the bulk properties (Li et. al., 2012, Gogoi et. al., 2011,Sargunami and Selvakumar, 2007, Ömeroğulları and Kut, 2012). The most attractive aspect of plasma-based surface treatments is that several gasses can be used to produce plasma, such as oxygen, nitrogen, argon, helium, carbon dioxide, fluorine, CF4, SF6 and air (Li et. al., 2012). Low-temperature plasma is widely used as an effective treatment method in porous textile materials due to its high penetration into entire textile structure and effective etching functions on surfaces of all single fibers. Plasma penetration into the textile structure or active particles moving through the entire fabric thickness, can only occur with the mean free path of excited species above the typical distance between fibers in fabric (Long et al., 2008).

Another surface modification alternative is ozone treatment. Ozone is a powerful oxidizing agent with an oxidation potential of 2.07 eV (Sargunami and Selvakumar, 2006). Due to its high oxidation potential, ozone is very effective for water and wastewater purification Sargunami and Selvakumar (2006), Sargunami and Selvakumar (2007)and oxidative treatment of textile fibers. Several studies have been reported on ozone treatment of textile fibers; cotton Prabaharan et al. (2000), Perincek et. al. (2007),Eren and Öztürk (2011) polyester Eren et. al.(2012), jute Perincek et al. (2007), wool Ichimura et al. (2005), Perincek et. al.(2008), polylacticacid Eren et. al.(2011), nylon Avinc et. al. (2012) and silk Sargunami and Selvakumar (2011), Sargunami and Selvakumar (2012),Wakida et al. (2004), in the literature. Ozone treatments have the potential of savings in energy, time and water and also reduce the environmental impact (especially chemical oxygen demand values) of the processes (Eren and Anis, 2009). There have been studies on improving some properties of silk fabric with ozone and plasma treatments, these studies have been discussed by comparison of the results obtained at this study in the results and discussion section.

In this study, the effects of plasma and ozone treatments on the whiteness properties of silk fabric and the combined effect of ozone and plasma treatments on the physical properties of silk fabric has been examined. Ozone and plasma treatments were applied on the raw and degummed silk fabrics individually and also in combined order. The effects of individual and combined surface treatments on tensile strengths, yellowness and whiteness values of raw and degummed silk fabrics were determined with the required tests and SEM photographs were taken to characterize the treated surfaces.

2. EXPERIMENTAL

2.1. Material

100 % silk woven plain fabric, supplied by Ödemiş İpek Company (İzmir, Türkiye), was used in this study. The fabric weight was 50.8 g/m^2(36 warp/cm x 36 weft/cm).

Genbleach CPB30, supplied by Genkim Company (İstanbul, Türkiye) which contents H_2O_2 and $NaHCO_3$ were used through degumming process to remove sericin from raw silk fabrics.

2.2. Degumming Process

Degummed silk fabric was obtained by removing sericin through a degumming process, involving boiling the raw silk fabric at a liquor ratio of 60:1 with 5-7 g/L Genbleach CPB30 and 2 g/L $NaHCO_3$ at 95 ^{0}C for 60 min. After thoroughly washing with warm water, the degummed silk fabric was dried at room temperature (25 ^{0}C).

2.3. Low Frequency Plasma Process

Since the surface modifications achieved by low pressure plasma are more uniform and has been controlled better than atmospheric plasma, experiments were performed on both raw and degummed silk fabrics with vacuum plasma device (Diener, Germany). As oxygen plasma treatment has a good modification effect and improves the hydrophilic characters of many fabrics in numerous researches Ömeroğulları and Kut (2012), Morent et al.(2008), all silk fabrics were modified with oxygen gas in the plasma treatment. After the available oxygen gas was discharged into the vacuum chamber, the samples were placed in and treated with LF (Low Frequency) generator at a frequency of 40 kHz, at a power of 100 W, at a pressure of 200 Pa with three exposure times (5,10,15 min) and at low temperature (40 ^{0}C). The oxygen gas flow rate was 60-65 sccm. In order to determine the modification effects of plasma treatment and variations in surface characterization of samples after treatment, exposure times were varied in this study. On the purpose of indication the oxygen plasma effect on silk fabrics (both raw and degummed silk fabrics), some of the samples were treated with only oxygen plasma at these conditions without being applied with ozone later. However, some of the silk fabrics were treated at these plasma conditions before and after ozone treatment to investigate the combined effect of plasma and ozone treatment together.

2.4. Ozone Treatment

All ozone treatments were performed with an OS1 (Opal, Türkiye) model ozone generator at room temperature at a liquor ratio of 20:1. Ozone concentration was measured according to the Standard Iodometric Method (APHA, Standard Methods, 2350E, 19th Edition, 1995). The ozone mass flow in the outlet gas of the ozone generator was measured as 6.6 mg/min at the adjusted gas-flow rate by feeding high purity oxygen into the ozone generator. The ozonated silk fabrics were immediately rinsed under tap water with stirring for 2 min in order to remove residual ozone. The exposure times were varied similarly to plasma treatment mentioned above. Raw and degummed silk fabrics were ozonated for 5, 10 and 15 min.

2.5. Treatment Sequence

At the first stage of the experiments, plasma and ozone treatments were individually applied to the silk fabric samples for 5,10 and 15 min. At the second stage of the experiments, plasma and ozone treatments were applied to raw and degummed silk fabric samples in combined order, which includes ozone treatment after plasma or plasma treatment after ozone. The treatment times of combined order for each surface treatment were also 5, 10 and 15 min.

The experimental set-up is shown below in Table 1.

Table 1. Experimental set-up

The types of treatments	*The treatment time*	*Raw silk*	*Degummed silk*
		Samples	*Samples*
Only plasma treated samples	5 min.	R5 (P)	D5 (P)
	10 min.	R10 (P)	D10 (P)
	15 min.	R15 (P)	D15 (P)
Only ozone treated samples	5 min.	R5 (O)	D5 (O)
	10 min.	R10 (O)	D10 (O)
	15 min.	R15 (O)	D15 (O)
First plasma and then ozone treated samples	5 min.	R5 (P+O)	D5 (P+O)
	10 min.	R10 (P+O)	D10 (P+O)
	15 min.	R15 (P+O)	D15 (P+O)
First ozone and then plasma treated samples	5 min.	R5 (O+P)	D5 (O+P)
	10 min.	R10 (O+P)	D10 (O+P)
	15 min.	R15 (O+P)	D15 (O+P)

(P): Plasma treated *(P+O): Plasma and ozone treated* *D: Degummed*
(O): Ozone treated *(O+P): Ozone and plasma treated* *R: Raw*

2.6. Yellowness and Whiteness Values

CIE L*, a*, b* and ΔE values, whiteness and yellowness indexes of untreated and treated silk fabrics were investigated by a Spectrophotometer (Konica Minolta CM-3600 d, Japan) in order to determine the effects of plasma and ozone treatments on the changes in whiteness and yellowness values.

2.7. Tensile strength analysis

Tensile strengths of the silk fabrics were measured by an Universal Testing Machine (Instron Model No. 4301, U.S.A.) with a gauge length of 100 mm and a crosshead speed of 100 mm/min.

2.8. Scanning electron microscope analysis

The surface morphology of untreated and treated silk fabrics were scanned by a (ZEISS/EVO 40, Germany) electron microscope at 10 kV under a high vacuum at 2000 magnification after being coated with gold-palladium (Au-Pd) at a thickness of 40–50 nm by a BAL-TEC SCD 005 coating device.

3. RESULTS AND DISCUSSION

3.1. Yellowness and whiteness results

The CIE L*, a*, b* and ΔE values, whiteness and yellowness indexes of raw silk fabrics after 5, 10 and 15 min. plasma and ozone treatments are shown in Table 2. According to the results, it can be clearly seen that all the values of ΔE are smaller than 1, except sample R15 (P) (plasma treated for 15 min.) and sample R15 (P+O) (the combined treatment of plasma and ozone for 15 min). Consequently, it can be understood that plasma and ozone treatments lasting less than 15 min. did not cause significant ΔE changes of raw silk fabrics even if they are applied in combination or not. It was reported in the literature Fang et al. (2008) that low temperature oxygen plasma treatment increases the roughness of surface of silk fabric. Moreover, it is also determined that increasing the time of oxygen plasma treatment increases the roughness of the surface of silk fabric (Fang et al., 2008). It is considered in our study that ΔE changes are occurred because the amount of reflected fraction of lights from the treated rough surfaces of silk fabrics are decreased when compared with untreated smooth surfaces due to increasing the roughness of surfaces by low temperature oxygen plasma treatment which is in agreement with the results of the research (Fang et al., 2008). As seen in Table 2, R5 (O), R10 (O) and R15 (O) samples do not exhibit a considerable change either in whiteness or yellowness values compared to the raw sample. A slight increase occurred in whiteness of 5 min ozonated sample R5 (O) (57.2 to 59.3), yellowness of the same sample R5(O) also decreased (from 15.4 to 14.6) parallel to the increase in whiteness. The whiteness and yellowness values of the 10 and 15 min ozonated samples R10 (O), R15 (O) remained almost the same with that of raw silk sample. However, the yellowness indexes of ozone treated silk fabrics are generally higher than plasma treated fabrics. It is considered that oxidation of amino acid residues, especially glycine, alanine, serine and tyrosine increase the yellowness owing to the formation of chromophoric products containing carbonyl groups (Sargunami and Selvakumar 2006, Sargunami and Selvakumar 2007).

When the whiteness indexes are examined, it can be seen that plasma treatment applied individually lasting more than 5 min. causes more increase in whiteness of raw silk fabric compared to ozone treatment. Moreover, the smallest whiteness indexes are belonging to ozone treated fabrics which were plasma treated firstly. When the time of ozone treatment is increased, whiteness is decreasing whereas yellowness is increasing. So, it seems ozone treatment is more effective on decreasing whiteness and increasing yellowness of raw silk than plasma treatment. Since the oxidation potential of ozone (2.07 eV) is much higher than that of oxygen (1.23 eV), it is considered that ozone can drive oxidation processes much faster than oxygen alone (*www.differencebetween.com/difference-between-oxygen-and-vs-ozone/* and *www.infrasoil.nl/Afbeeldingen/Perozone/FlyerA4.pdf*). Additionally, in low-temperature plasmas, the temperature of ion is so small (0,03 eV) that it is considered to be negligible and the thermal energy of the neutral atoms and molecules stay roughly at room temperature; whereas the free electrons can transmit high energy. When the energy characteristics of oxygen atom or molecule in low temperature plasma are investigated, it can be seen that the electron affinity of O is 1.5 eV whereas O_2 has 0.45 eV electron affinity (Shishoo, 2007).

Furthermore, slight decrease (3.8 % after 10 min ozonation) of the yellowness index of raw silk fabric after ozone treatment has been reported in the literature (Sargunami and Selvakumar, 2007). The percent decrease of the yellowness index for the 5 min ozonated sample R5 (O) is approximately 5 % and this is in agreement with the results of the former research of Sagrumani and Selvakumar, (2007). However, the yellowness index adversely increased (and the whiteness values decreased) after prolonged ozone treatments of 10 and 15 min. The reason for the yellowing is attributed to the formation of carbonyl groups and formyl kynurenine (Sargunami and Selvakumar, 2007).

According to Table 2, combination of ozone and plasma treatments respectively for 5 and 10 min. increases the whiteness indexes of raw silk fabric. However, the whiteness indexes of them are decreased when the treatment time of combination is 15 min or the sequence of treatments was changed to opposite. When the sequence of treatments was compared to each other, it can be seen the whiteness indexes of R(O+P) is slightly more than the whiteness indexes of R(P+O) in each three treatment time. As we mentioned above that ozone treatment is more effective on fabrics surface due to its powerful oxidizing effect, the silk fabric was more affected by the ozone treatment after having a treatment of oxygen plasma. When the etched silk surface which treated by charged oxygen atoms, electrons and ions produced by the plasma treatment meets the O_3 in an aqueous media, the surface is much more affected by ozone treatment.

Table 2. The CIE L*, a*, b* and ΔE values, whiteness and yellowness indexes of raw silk fabrics after plasma and ozone treatments

Samples	CIE Lab Values			ΔE	Stensby (Whiteness Index)	ASTM D1925 (Yellowness Index)
	L*	a*	b*			
Raw silk	82.072	-0.726	6.998		57.204	15.439
R5 (P)	81.943	-0.568	6.366	0.664	59.123	14.331
R10 (P)	82.411	-0.515	6.122	0.976	60.410	13.830
R15 (P)	82.407	-0.387	6.045	1.400	60.965	13.782
R5 (O)	81.526	-0.349	6.365	0.821	59.295	14.575
R10 (O)	81.917	-0.483	6.996	0.707	57.748	15.518
R15 (O)	81.651	-0.481	7.085	0.495	57.226	15.886
R5 (P+O)	81.939	-0.770	7.266	0.361	56.257	15.953
R10 (P+O)	82.309	-0.912	7.641	0.738	55.001	16.519
R15 (P+O)	80.754	-0.898	7.371	1.414	54.306	16.198
R5 (O+P)	81.759	-0.292	6.504	0.777	59.353	15.523
R10 (O+P)	82.280	-0.433	6.465	0.899	59.736	14.601
R15 (O+P)	81.618	-0.514	7.482	0.707	56.119	17.099

Table 3 shows the results of CIE L*, a*, b* and ΔE values, whiteness and yellowness indexes of degummed silk fabrics after 5, 10 and 15 min. plasma and ozone treatments. According to the results, plasma and ozone treatments cause significant changes in ΔE of degummed silk fabrics. The values of ΔE of all the treatments used ozone, are much higher than only plasma treated ones. Moreover, the increase in yellowness indexes of ozonated degummed silk fabrics is more significant than the values of ozonated raw ones. It is considered according to literature Sargunami and Selvakumar (2007) that these changes are attributed to chromophoric products containing carbonyl groups mainly from tyrosine which increase yellowness especially after ozone treatment of degummed silk fabrics.

Table 3. The CIE L*, a*, b* and ΔE values, whiteness and yellowness indexes of degummed silk fabrics after plasma and ozone treatments

Samples	CIE Lab Values			ΔE	Stensby (Whiteness Index)	ASTM D1925 (Yellowness Index)
	L*	a*	b*			
Degummed silk	84	-0.821	4.629	0	64.983	10.421
D5 (P)	82.663	-0.545	6.171	1.946	60.474	13.874
D10 (P)	82.112	-0.618	5.691	1.854	61.039	12.800
D15 (P)	84.348	-0.513	5.709	1.288	63.526	12.794
D5 (O)	82.610	-0.895	8.111	3.818	54.642	17.286
D10 (O)	82.642	-1.035	7.734	3.327	55.319	16.552
D15 (O)	81.829	-1.121	6.716	2.994	56.579	14.579
D5 (P+O)	80.954	-0.891	7.071	3.764	55.355	15.629
D10 (P+O)	84.035	-1.367	7.849	3.433	55.319	16.332
D15 (P+O)	82.757	-0.669	5.958	1.980	60.743	13.366
D5 (O+P)	80.417	-0.796	6.492	4.020	55.830	15.156
D10 (O+P)	80.765	-0.812	7.060	3.906	55.410	15.690
D15 (O+P)	81.344	-1.240	8.973	5.031	50.024	19.002

Yellowness and whiteness indexes of raw and degummed silk fabrics are shown in Fig.3 and Fig. 4. It seems that ozone treatments are more effective than plasma treatments on decreasing the whiteness indexes and increasing the yellowness indexes of degummed silk fabrics and this effect is more notable than the raw ones. It is attributed to powerful oxidation effect of ozone compared to plasma and the breaking of the polypeptide chains in the fibroin structure faster than in the raw silk fabrics because of the absence of sericin. When the combination of two treatments were carried out, increases in yellowness indexes and decreases in whiteness indexes of degummed silk fabrics were more significant due to the double oxidization effect of treatments.

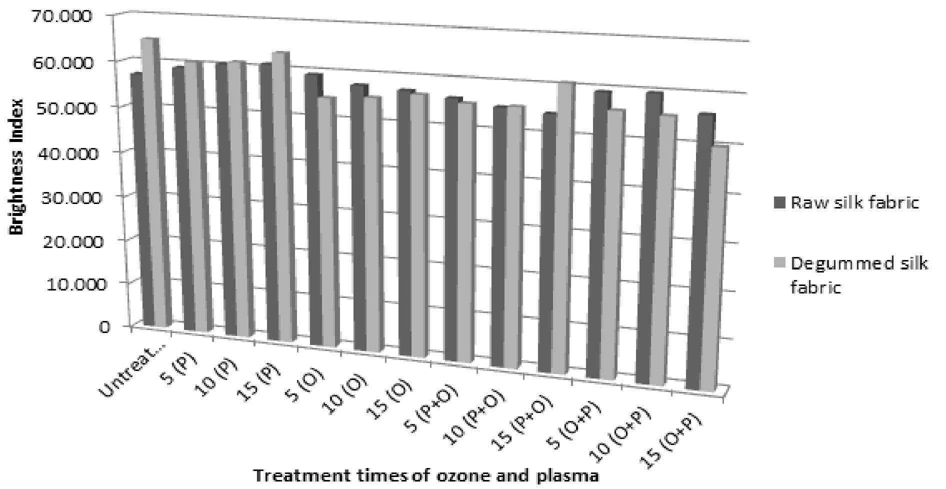


Figure 3:
Whiteness indexes of untreated and treated raw and degummed silk fabrics

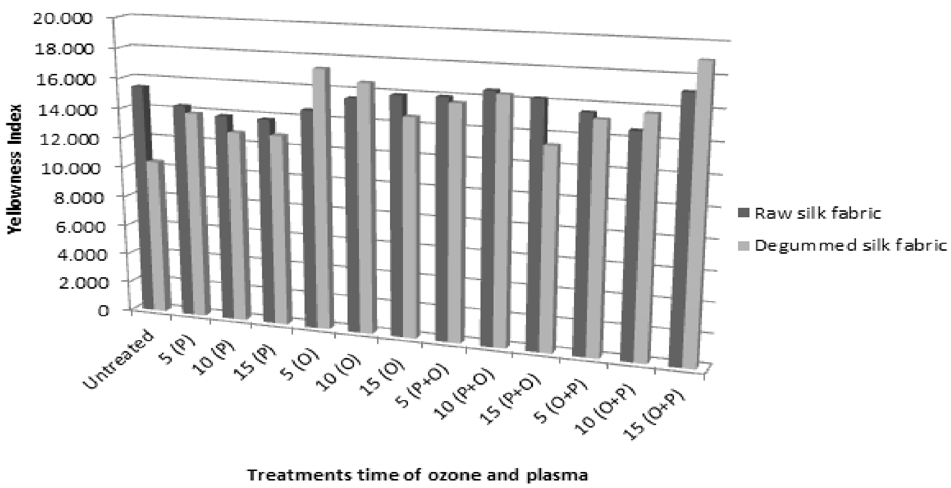


Figure 4:
Yellowness indexes of untreated and treated raw and degummed silk fabrics

3.2. Tensile strength results

The tensile strength results of raw and degummed silk fabrics after plasma and ozone treatments are shown in Table 4. After these treatments, there was an increase in breaking strengths of raw silk fabrics whereas decrease was occurred in breaking strengths of degummed silk fabrics. The main difference of fibroin and sericin structure is the amount of amorphous and crystalline molecules of them are not same; sericin is amorphous structured whereas nearly 60 % of region of fibroin is crystalline structured. Fibroin macromolecules do not possess helix structure due to the presence of beta-structure instead of alpha. That's why, lots of H-bonds can be observed between macromolecules (Tarakçıoğlu, 1983). Thus, it can be mentioned that the ozone and plasma treatments applied to raw silk fabrics, do not affect the fibroin structure in the raw silk fabric so that the H-bonds and the crystalline structure of it is not disintegrated by the surface treatments. However, the fibroin structured of degummed silk fabrics is hydrolyzed by the ozone and plasma treatments since it has no longer sericin on its surface. The decrease in tensile strength of degummed silk fabrics was more significant when ozone treatment was applied. It is considered that reason of tensile strength decrease was attributed to the rupture of fiber macromolecules.

As the plasma treatment only modifies the outermost thin layer of the surface, while the bulk properties will be kept untouched, the amorphous sericin layer was the only material when the surface treatments etched on the raw silk fabrics. Because plasma methods result in a notable etching effect from physical bombardments and chemical reactions by excited plasma species on sericin layers (Kalantzi et. al, 2013). As mentioned in the research by Long et.al. (2008), not constantly but in some parameters of plasma treatment, there was some increase in tensile strength of raw silk fibers when the discharge power and the treatment time of plasma was increased. According to the authors, these increases are attributed to the cross linking reactions happened between sericin and/or fibroin chains during plasma treatment. Thus, in our research, the increasing results in the tensile strength of raw silk fabrics during the surface treatments are probably due to the result of cross linking reactions on fabric surface.

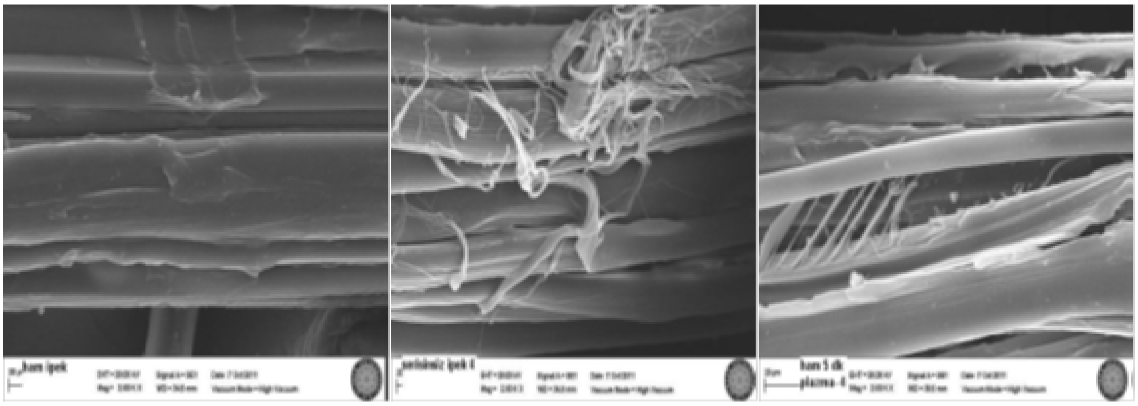
However, decreases in tensile strengths were occurred when the ozone and plasma treatments were applied on the degummed silk fabrics. The fibroin, crystalline structured and rich in glycine (43.7%), alanine (28.8%) and serine (11.9%), is composed of heavy chain (~325 kDa), a light chain (~25 kDa) and a glycoprotein. The heavy chain contains very long stretches of Gly-X repeats that consist of 12 repetitive domains (Kalantzi et. al., 2013). As the glue-like sericin layer was removed from the surface of silk during degumming process, it is considered that the crystallinity of fibroin structure was decreased due to the polypeptide chain was broken and macromolecule recombined Yu-yue (2004) during the oxidant treatments used in this research. SEM results were also a kind of evident the tensile results. Some fibrillations of the degummed fabrics after plasma and ozone treatments were clearly seen on the SEM photographs whereas, any fibrillations of the raw fabrics which treated with ozone and plasma, could be seen on the SEM photographs.

Table 6. The tensile strength values of raw and degummed silk fabrics after plasma and ozone treatments

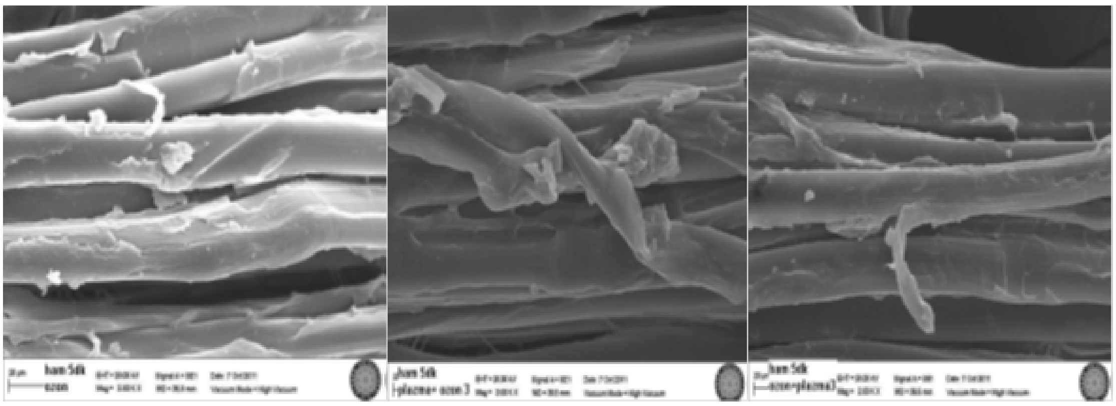
Raw silk fabrics	Maximum Load (kN)	Degummed silk fabrics	Maximum Load (kN)
Raw silk	0.2720	**Degummed silk**	0.2953
R5 (P)	0.3027	**D5 (P)**	0.2904
R10 (P)	0.2905	**D10 (P)**	0.2844
R15 (P)	0.3137	**D15 (P)**	0.2204
R5 (O)	0.3048	**D5 (O)**	0.2640
R10 (O)	0.3254	**D10 (O)**	0.2660
R15 (O)	0.3244	**D15 (O)**	0.1669
R5 (P+O)	0.2571	**D5 (P+O)**	0.2170
R10 (P+O)	0.2790	**D10 (P+O)**	0.2247
R15 (P+O)	0.2969	**D15 (P+O)**	0.2143
R5 (O+P)	0.3501	**D5 (O+P)**	0.2146
R10 (O+P)	0.3506	**D10 (O+P)**	0.2945
R15 (O+P)	0.3031	**D15 (O+P)**	0.2261

3.3. Results of SEM analysis

According to the SEM photographs at 2000 magnification (Fig.6), it can be clearly seen that untreated raw silk fabric has a smooth surface whereas fibrillation is occurred on degummed silk fabric due to removing glue-like layer, sericin, which keeps the fibroin macromolecules together. When plasma and ozone treatment were applied on raw silk fabric one by one, roughness can be seen in both of them. When these treatments were applied in combined order, fibrillation, peeling and breaking of fibers can be seen especially in the SEM photographs of treated and degummed silk fabrics. The most fibrillation and surface modification are seen in SEM photograph of fabrics which treated with plasma and ozone in a combined order due to double surface treatments.

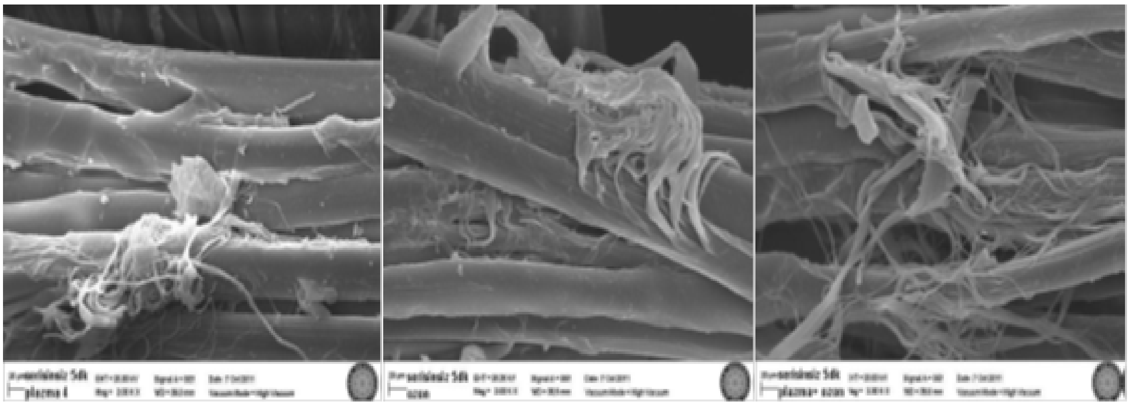


a. *Untreated raw silk fabric* ***b.*** *Untreated degummed silk fabric* ***c.*** *R5 (P)*

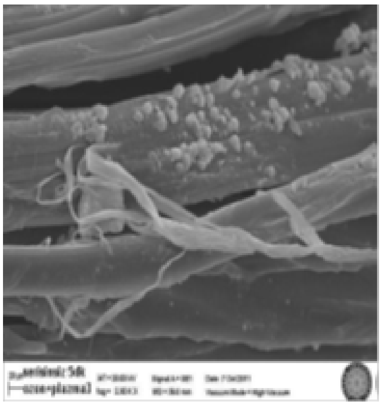


d. *R5 (O)* ***e.*** *R5 (P+O)* ***f.*** *R5 (O+P)*

Figure 6:
SEM photographs of untreated and treated silk fabrics



***g.** D5 (P)* ***h.** D5 (O)* ***j.** D5 (P+O)*



***h.** D5 (O+P)*

Figure 6 (continued):
SEM photographs of untreated and treated silk fabrics

4. CONCLUSIONS

In this study, raw and degummed fabrics were treated with plasma and ozone as a pre-treatment for 5, 10, 15 min. These pre-treatments were applied on silk fabrics one by one and also in combined order. In some applications of our study, treatment was started with plasma, and then went on with ozone treatment whereas in some of other applications the opposite order was used in order to determine the combined effect of surface treatments on raw and degummed silk fabrics. According to the results, plasma and ozone treatments did not cause significant ΔE changes of raw silk fabrics whereas notable ΔE differences were occurred on the degummed silk fabrics which were pre-treated with plasma and ozone. The treatment time took an important part, especially in combined order of surface treatments. Generally, when time is increased, increase of yellowness and decrease of whiteness were clear. According to our research, from the point of increasing the whiteness indexes (decreasing the yellowness indexes) with enhanced tensile strengths of raw silk fabrics, applying plasma treatment was better than applying ozone treatment individually. From the same point of view, it was determined that applying silk fabrics with ozone treatment after plasma, especially for 10 and 15 min. was the worst combination among the others.

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